Photocatalytic reforming of glycerol for the production of hydrogen under ambient conditions

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Introduction

Glycerol is an abundant feedstock which has great potential for use in a number of chemical conversion routes to generate high-value products. The upgradation of glycerol from processes such as biodiesel production could potentially increase the economic viability of the bio-refinery industry. Photocatalysis presents an alternative method to current approaches, which is environmentally benign and can operate under favourable ambient conditions. Using a metal oxide, illumination of a specific wavelength can be used to induce photo-redox reactions. In this instance, glycerol can undergo oxidation to products such as 2-dihydroxyacetone, while protons are reduced to form H_2. Presented here is the development of a thin film photocatalytic reactor capable of reforming glycerol to H_2 under low power UV irradiation.

Materials and Methods

The Pt-TiO_2 catalyst was prepared based on a method reported by Mills *et al.*[1]. A TiO_2 paste was synthesised following a sol-gel process starting with a titanium (IV) isopropoxide precursor and coated onto borosilicate glass columns. Platinum was photo-deposited onto the TiO_2 coated tubes by irradiating a solution of dihydrogen hexachloroplatinate (IV) hydrate ($H_2PtCl_6.6H_2O$) methanolic solution. The photocatalytic recirculating system consisted of a feed tank, peristaltic pump and an illumination unit (Figure 1). The feed tank was a propeller fluidised photo reactor (PFPR) (reported elsewhere by Skillen *et al.*[1]). The illumination unit consisted of four 8 W UV black lamps (Philips) with a peak wavelength emission at 365 nm. In a typical experiment, a glycerol solution was prepared and placed inside the PFPR. The entire system was purged with N_2 for 30 min prior to any irradiation to eliminate the presence of O_2. Following this, the pump was started and allowed to completely recirculate before the lamps were switched on. During illumination gas samples (100 µL) were extracted from the headspace of the PFPR via a syringe port at given time points and analysed by GC-TCD. The detection of H_2 was determined by comparison to a standard injection of pure H_2, while quantification was determined from a calibration of known concentrations.

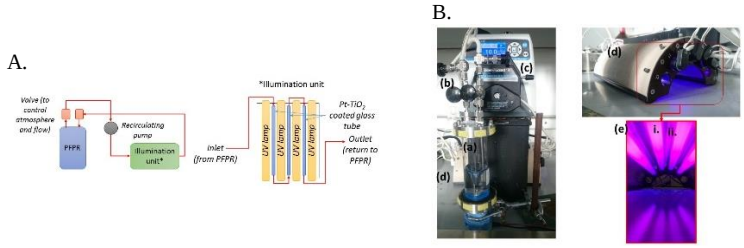

Figure 1. *A. Schematic representation of the reactor and B. Images of the reactor showing (a) the PFPR feed tank, (b) valves that control the atmosphere and flow in the unit, (c) peristaltic pump (d) illumination unit and (e) an internal image of the illumination unit with i. the black lamps and ii. the coated tubes.*

Results and Discussion

Under ambient conditions, Pt-TiO_2 coated onto a glass column solid support showed impressive reforming of glycerol to generate H_2 over a small catalyst surface area. Figure 2 shows the typical profile of H_2 evolution when illumination is switched on and off along with the recyclability of the catalyst coating. During dark periods, no H_2 production was recorded indicating this was a photo-induced reduction reaction. The continued and linear evolution of H_2 after purging highlights the stability and reproducibility of the catalyst film.

Figure 3 shows the impact of feedstock flow rate on the evolution of H_2. From an engineering viewpoint, the performance of a photocatalytic system is typically dictated by both light penetration and mass transfer. Controlling the flow rate in this system allowed mass transfer limitations to be reduced while ensuring H_2 generated on the catalyst surface was recirculated to the site of analysis (PFPR gas headspace). The results show that at 40 ml min^{-1} an optimum point was reached (max reaction rate = 0.0026 µmole min^{-1}), while increasing beyond this point demonstrated that mass transfer limitations no longer predominate and H_2 evolution decreased.

The rate of H_2 presented here is significant considering the available catalyst surface area was only 59.19 cm^2, giving a rate of ~0.003 µmole H_2 cm^{-2}. Moreover, using a modular system such as the one shown here can potentially allow for feasible scale up while maintaining the efficiency shown. This is advantage not seen with traditional slurry/suspended systems.

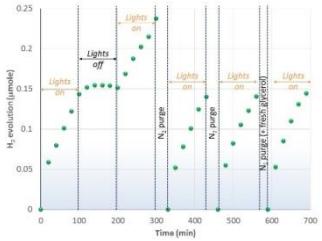

Figure 2. *Evolution of H_2 as a function of irradiation time, demonstrating continued production during illumination and recyclability of the catalyst*

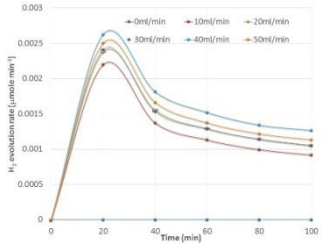

Figure 3. *H_2 evolution rate as function of irradiation time and feedstock recirculation speed*

Significance

To date, there have been no examples reported in the literature of a thin film photo-reactor capable of generating H_2 from a glycerol feedstock, which highlights the significance of the work presented here. The immobilised reactor was capable of photocatalytically reforming glycerol to H_2 under ambient conditions using a Pt-TiO_2 catalyst. This study demonstrates the evolution of H_2 despite using low power irradiation (8 W) and a fixed catalyst with a reduced surface area. Controlling both the inlet concentration of glycerol and the speed at which the feedstock passes through the unit allows for an increased production rate (0.0026 µmole H_2 min^{-1}) to occur. As previous studies have focused on conversion using a powder catalyst, the development of this system provides a significant platform to investigate the feasibility of a scaled up unit.

References

1. Mills, A. *et al. Photochem. Photobiol. Sci.* **2003**, *2* (5), 591
2. Skillen, N. *et al. Chemical Engineering Journal.* **2016**, 286, 610-621